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Cast and investigate the characteristics of a high strength aluminium, copper and silver alloy

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Abstract

This is an investigation into the effect of adding pure silver to a 'duralumin' type alloy and its impact on hardness and strength. The alloys were produced as small cuboid ingots by gravity casting into graphite molds and cooling in air. The silver content added ranged from zero to 10 per cent by weight. The following consecutive stages were used; casting; homogenisation, solution treatment, ageing for 2 hours and ageing for 4 hours. Post-casting the alloy ingots were heat treated simultaneously to ensure all samples had been subjected to the same conditions. After each stage of the investigation a slice was taken from each sample and mounted in Bakelite. The mechanical property of hardness was investigated by means of a Vickers hardness tester. The materials' microstructure was examined under both an optical microscope and a scanning electron microscope in order to further understand the mechanisms that had contributed to the increase in the material's strength. It was found that strength and hardness increased with silver content up to 10%. And a principle mechanism that caused this was the formation of precipitates in the materials' microstructure.

Introduction

Overview

Engineers have been aware of the improvements to material properties such as strength and hardness that ageing brings since the chance discovery of the phenomenon by the German metallurgist Alfred Wilm in the early 20th century (Wilm, 1911). This led to the development of the much used 'duraluminium' type aluminium, copper and magnesium alloys.

Wilm found that the improvement in strength and hardness stems from solid solution strengthening as well as the formation of non-equilibrium phases in the material's microstructure. Other material properties were affected; corrosion resistance, as well as temperature dependent properties such as creep resistance and fatigue resistance.

Early work by Ueno (Ueno & S, 1930) focused on the phase relations present in the ternary system under consideration using ideas developed by Josiah Willard Gibbs in the late 19th century.

A thermodynamic evaluation of the Al, Cu, Ag ternary system identified three eutectic phases in the equilibrium state; aluminium in solid solution with the other two constituents (denoted α), a copper and aluminium phase, CuAl_2 , (θ) and a silver and aluminium phase, Ag_2Al , (γ) (Witusiewicz et al., 2005).

However, this study relates to equilibrium phases in the ternary system in question. The present study examines an aged alloy which by definition is not in a state of equilibrium.

Materials and experimental procedure

Materials used

The study investigates an experimental aluminium, copper and silver alloy with composition calculated by weight %. 11 alloys were prepared; every alloy contained 4 % copper by weight. The quantity of silver was varied from 0 to 10 % by weight, in steps of 1%, with the balance aluminium.

The materials used were 'pure' and were verified with an Olympus XRF hand-held x-ray device as having a purity of more than 99.99 %.

Sample preparation

The finished samples consisted of slices of polished and etched alloy mounted in Bakelite. The 11 alloys were produced with silver content from 0 to 10 % by weight.

A control alloy was produced containing no silver, with 4% copper and the balance aluminium by weight to provide a baseline against which to make comparisons.

Each was manufactured as a small gravity cast ingot, poured into graphite molds measuring 40mm x 30mm x 10mm.



Figure 1: Cast ingots next to 30cm rule for scale



Figure 2: Graphite mold used for gravity casting the ingots

Samples of each of the 11 alloys were prepared in five stages; as cast, homogenised solution treated, aged for 2 hours and aged for 4 hours. All stages were conducted at atmospheric pressure.

At each stage it was necessary to choose process parameters carefully. These included the temperatures and timings needed for solution treatment and those for homogenisation. Ageing temperatures and times were also needed. Quench rates (which depends on the quenching medium and its temperature) were also required to ensure maximum solid solubility was achieved during solution treatment.

After each of the five stages an 8mm cross sectional slice was taken, ultrasonically cleaned, and mounted in Bakelite. At each stage samples were carefully marked according to their silver content

The furnaces and kilns used for casting and heat treatment were fitted with programmable Euro-therm 3216 PID controllers. This allowed a suitable heat treatment profile to be designed and implemented for the stages of homogenisation, solution treatment and ageing (see appendix A6).

A method was developed for calculating the precise mass of each element for the mold volume using the elements' densities and eliminating two masses to leave the required mass of a single element (see appendix A2). This was done primarily to keep the cost of the research to an acceptable level and avoid waste.

All metal was ultrasonically cleaned before being cast. The following method was employed for casting; the kiln was heated to 1100 °C, 17°C above the melting point of pure copper (the constituent with the highest liquidus). The copper was added and the temperature of the unit given time to recover to ensure the copper was fully molten.

A master alloy was then prepared consisting of equal quantities by weight of copper and aluminium, before the remaining material was added

Once all the material had formed a fully molten liquid solution it was stirred using a graphite rod. Ten minutes was given for natural diffusion to occur and the solution was agitated once more with the rod, before pouring the liquid alloy under gravity into graphite molds. The resulting ingots were cooled in air before being stamped with a number reflecting the intended silver content.

The kiln was thoroughly cleaned of residual alloy before the process was repeated once more for the next alloy.

Ingots were machined flat and square to save polishing effort before being sliced through to give a sample that covered the whole cross –section of the alloy.

55 samples in all were prepared (11 at each of the 5 stages) including the control alloy of duraluminium type with no silver.

All were etched with Keller's etchant after following standard grinding and polishing procedures prior to final 0.04 μm colloidal silica polishing for a period of 15 min. The Keller's etchant attacked the silver aggressively, it was found.

The process parameters used for each stage are appended at A6. Ageing was carried out at 150 °C.

Sample analysis

The ingots were verified using an Olympus XRF hand-held x-ray machine. (the results of which are appended to this report at A3). This revealed that some of the ingots appeared to be very close to the intended constituents, but others were not.

Care was taken weighing the elements. Reasons for this discrepancy between what was found and intended include; verification was conducted before the homogenisation stage; the X ray gun examines a particular 'spot' on the material which may not have been representative of the whole. Averaging a series of readings across the material, and or using a larger spot size, may have given better results.

To build a better understanding of the microstructural evolution at the various stages, hardness testing, optical microscopy and SEM examination was conducted on the alloys at all stages. All electron microscopy was carried out using the Jeol 7001 FE SEM at the Plymouth Electron Microscopy Centre, at Plymouth University.

Results

Introduction

The graphs show hardness against silver content by weight for each of the 11 alloys that were manufactured and investigated. Hardness data at all 5 stages of the investigation are presented (as cast, homogenised, solution treated, aged 2 hours and aged 4 hours).

The first graph presented shows the trend-lines of all stages together to assist with comparing and interpreting the results.

Four hardness readings were taken across each sample at regular intervals across the sample surface for each stage. These four points are plotted below and a trend-line added.

The equation of the trend-line and its R^2 value are also presented. All the trend-line gradients lie between 1 and 3 showing a positive correlation between Ag content and hardness.

The R^2 values, which represents the statistical spread of the data, are much better for some trend-lines than others; placing this in context, some hardness readings were quite spread out across the same sample. For, example in the as cast state the hardness readings reading taken for the 9% Ag sample ranged from 78.4 to 49.2. For most of the samples the range of readings was much lower than this.

Comparison plot for all stages

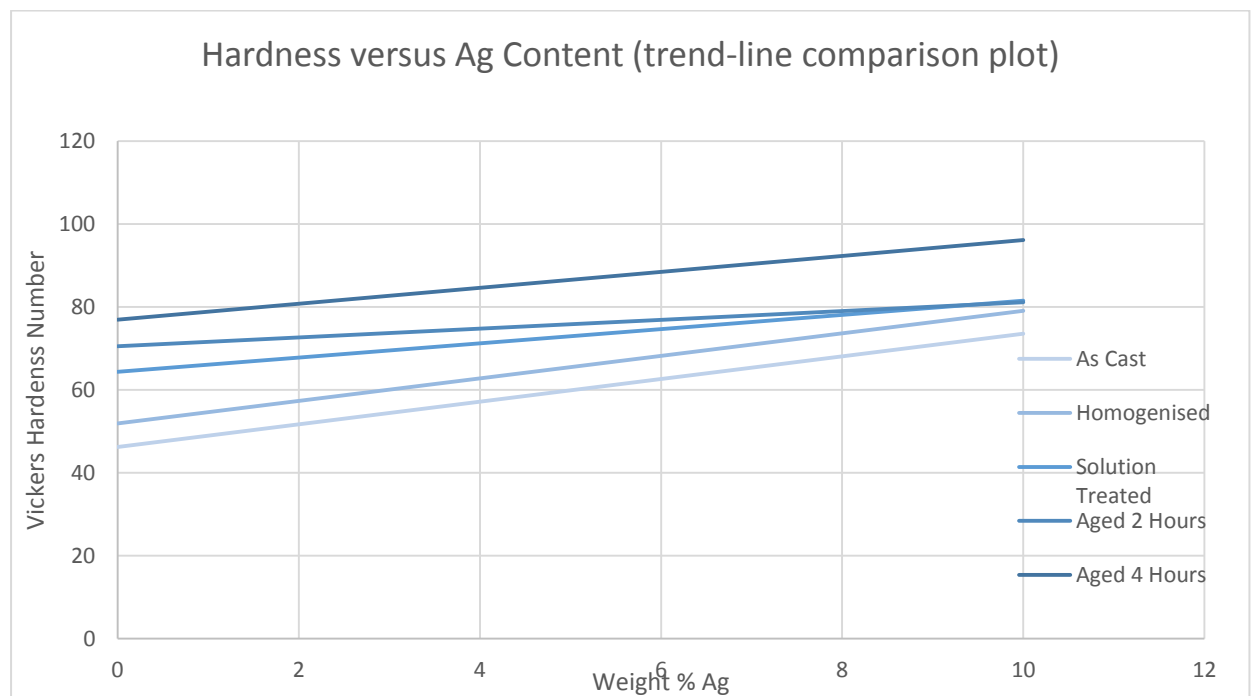


Figure 3: Trend-lines for all stages of the investigation for comparison

As cast hardness data

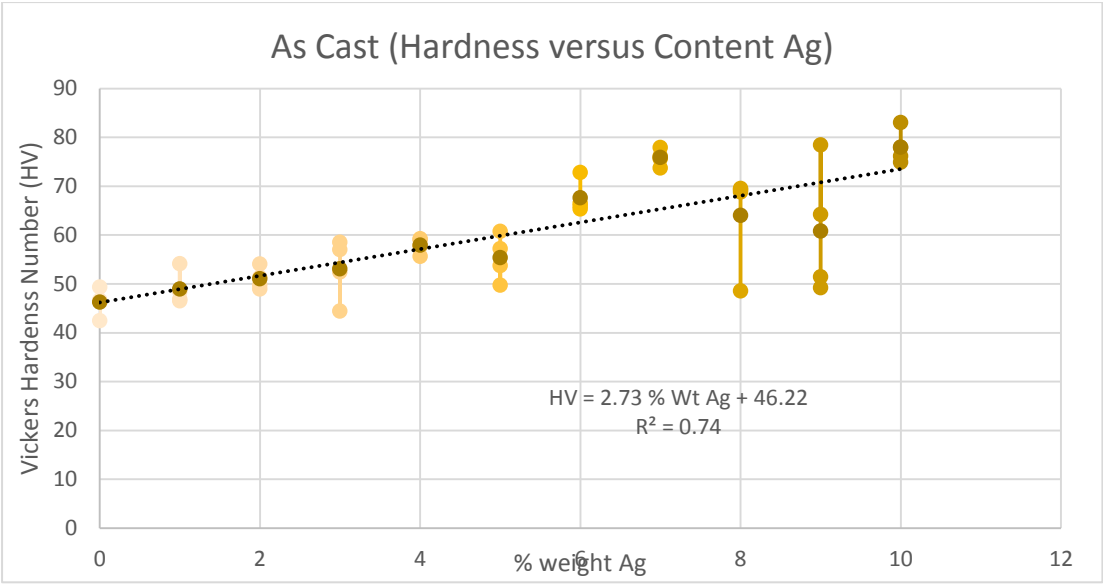


Figure 4: Graph showing hardness data collected for the As Cast samples

Homogenised hardness data

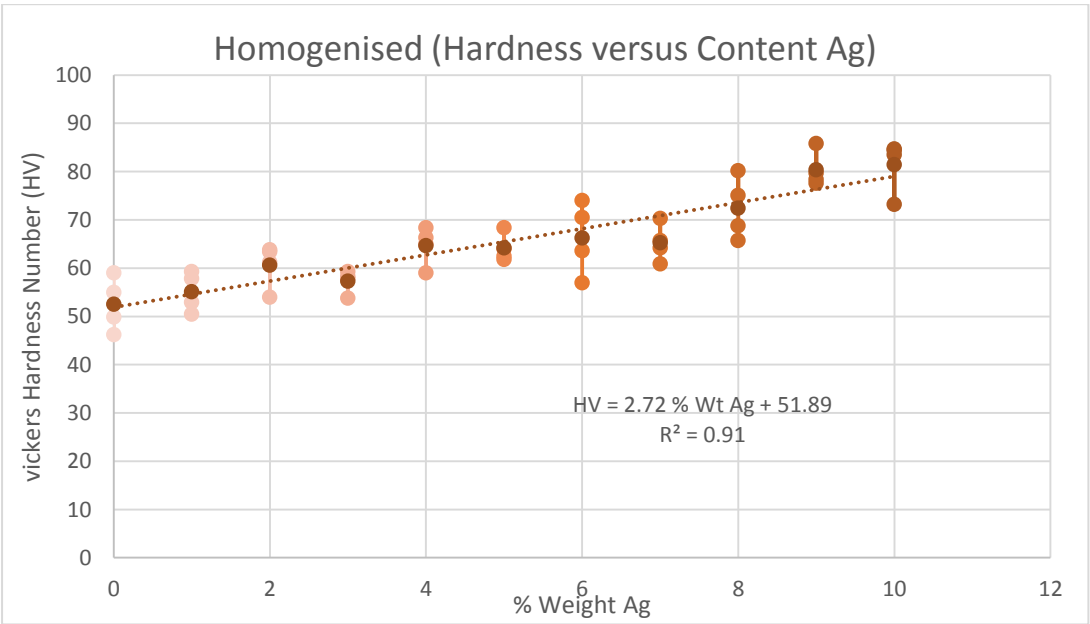


Figure 5: Graph showing hardness data collected for the homogenised samples

Solution treated data

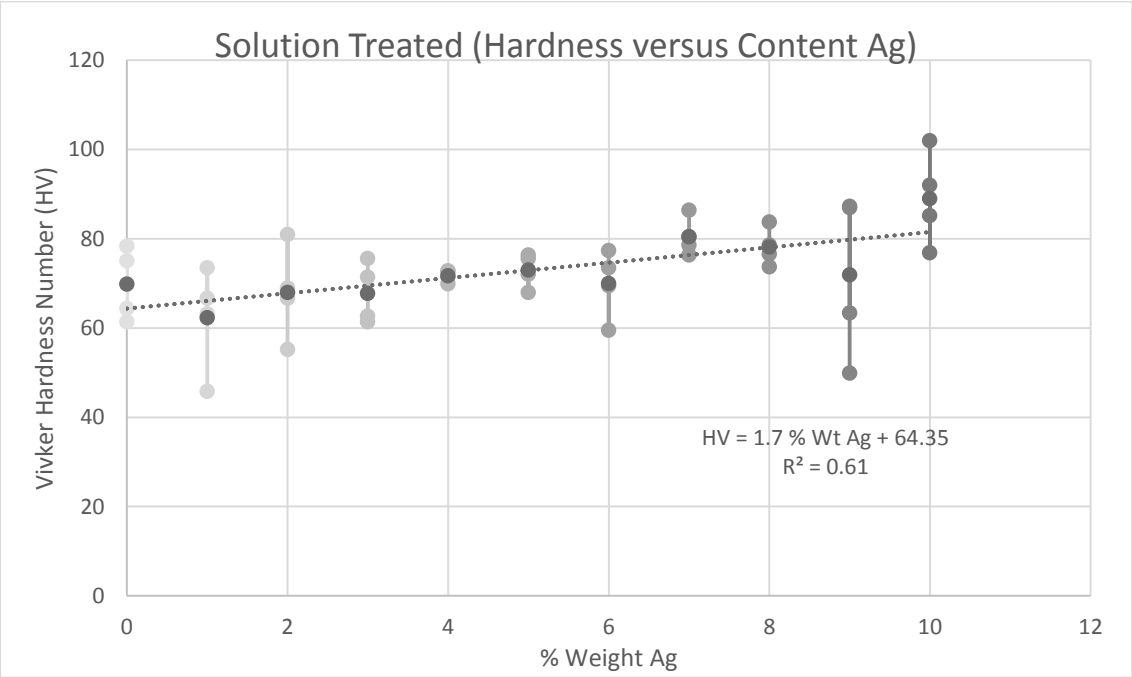


Figure 6: Graph showing hardness data collected for the solution treated samples

Aged 2 hours data

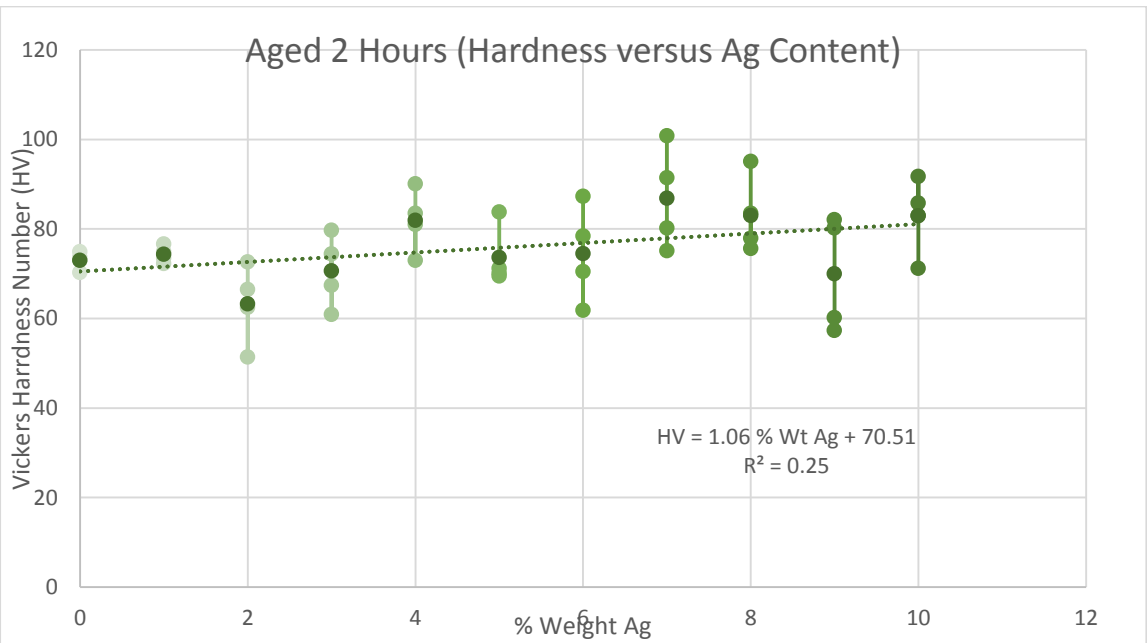


Figure 7: Graph Showing Hardness data collected for the samples Aged 2 Hours.

Aged 4 hours data

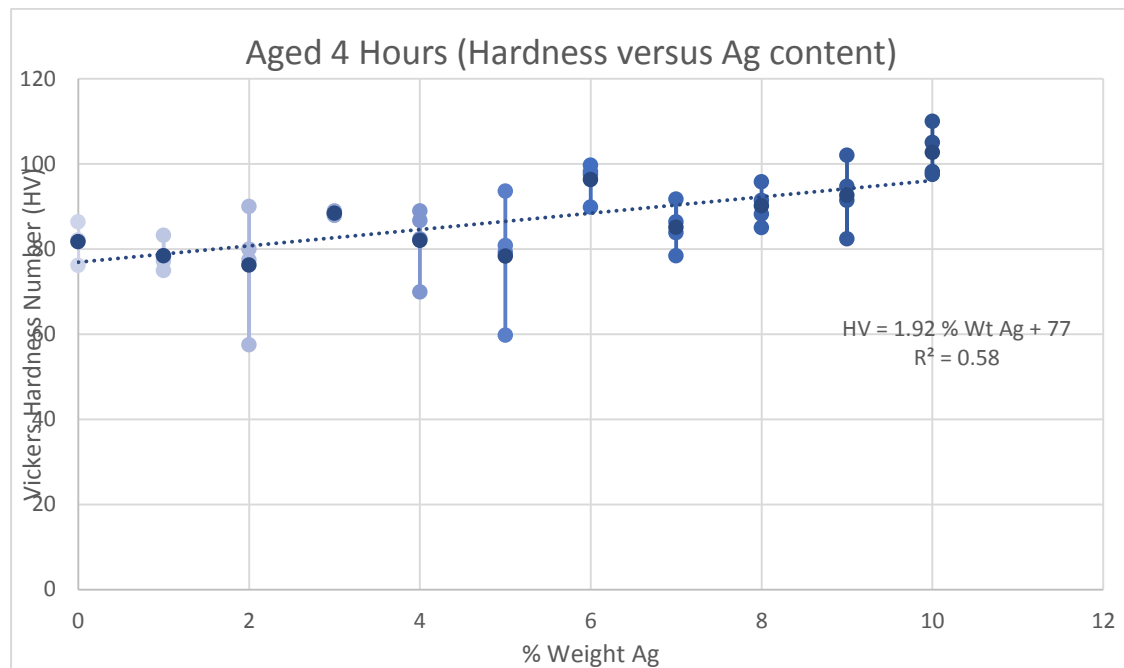


Figure 8: Graph showing hardness data collected for the samples aged 4 hours.

Material strength

Design choices are usually made by considering a material's strength rather than its hardness (Askeland 2011). The linear correlation between hardness and strength allows the results presented above to be easily interpreted in terms of the material's strength (both tensile and shear).

The graph below is intended to allow simple conversion of the hardness value reported into values for strength in MPa. The scale of the graph has been limited to the area of interest in the current study; the maximum hardness recorded in the study was around the 100 VHN mark.



Figure 9; Graph showing linear relationship between hardness and strength.

Discussion

Comparison of strength with other aluminium alloys

Broadly speaking the data presented above shows that hardness increased with silver content up to 10% by weight and that at each stage of the investigation hardness was improved.

The highest hardness reading in the investigation was recorded on the alloy aged for four hours with 10% Ag at VHN 110. This corresponds to a tensile strength of around 350 MPa. However, the average reading on this sample was around 290-300 MPa.

Tensile strength values for other heat treatable aluminium alloys are in the order of 300 – 600 MPa. A table showing the strength of some is presented below for comparison (Askeland, 2011).

It can be seen from the table that the values for the 10 % Ag sample aged for 4 hours (the strongest produced during this investigation) are significantly lower. However, it should be remembered that these other alloys are all manufactured in a wrought state (rather than cast) which significantly adds further strength due to strain hardening.

Table 1: Strength of common aluminium alloys

Designation	Content	Tensile Strength (MPa)	Shear Strength (MPa)	Condition
10% Ag (from this investigation)	Cu 4%, Ag 10%	290-300	160-200	cast
2024-T4	Cu 4%	469	324	wrought
2090-T6	2.4% Li, 2.7% Cu	552	517	wrought
4032-T6	12% Si, 1% Mg	379	317	wrought
6061-T6	1% Mg, 0.6% Si	310	276	wrought
7075-T6	5.6% Zn, 2.5% Mg	572	503	wrought

Ideally, a strong alloy has a continuous relatively soft matrix that provides ductility, with dispersed hard discrete precipitates to increase strength. This basic structure can be seen in this image of the 0% Ag (duraluminium type) sample aged for 2 hours manufactured in this investigation.

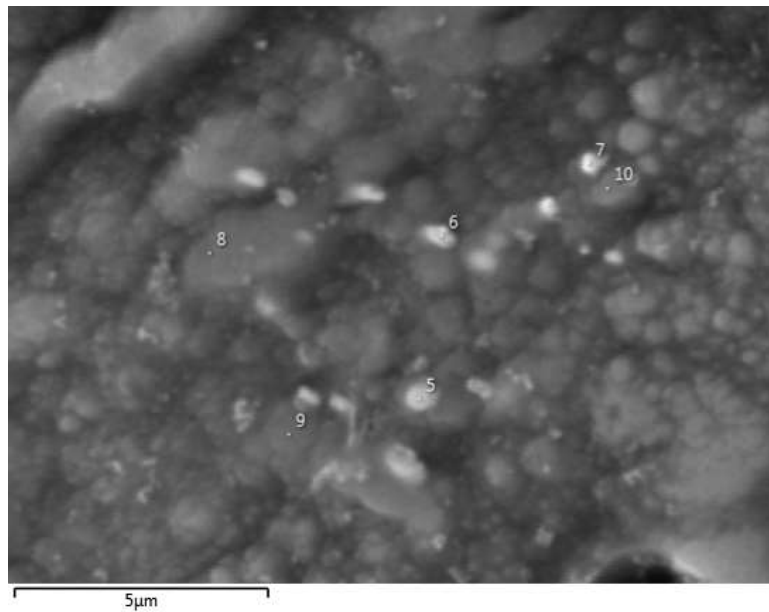


Figure 10; SEM image of sample with 0% Ag, 4% Cu, aged for 2 hours

It was taken with an electron microscope set in backscatter mode to highlight the copper rich precipitates. The numbered spots in the image are where X-ray back scatter has been used to determine the elements present and their percentage by weight.

The lighter rounded areas are copper rich precipitates with between 10 and 15% copper present. These hard rounded structures, denoted as the θ' phase in 2000 series aluminium alloys, are surrounded by a softer α phase. The darker α phase contains around 4% copper in a super-saturated solid solution, providing the ductile matrix for the much harder rounded precipitates.

Fracture mechanics has taught metallurgists that it is desirable the hard precipitates are rounded rather than sharp as this improves fracture toughness; the Griffiths equation, which models crack growth, shows that materials are more likely to fail if they contain discrete sharp precipitates (Zuidema *et al*, 2004).

Mechanisms of ageing

Polycrystalline metallic materials contain defects in the crystal lattice of three basic types; point defects, line defects and surface defects. All of these defects are of importance in the ageing process (Askeland, 2011).

Line defects, called dislocations, are one mechanism that gives ductility (another is grain boundary sliding). Ductility is desirable as it facilitates processes such as drawing and forging of crystalline materials. But ductile materials are not strong. The process of ageing aims to improve strength at the expense of ductility. Shear stress causes dislocations to pass through the material's structure, or 'slip' causing permanent strain otherwise known as plastic deformation.

Once the applied stress exceeds the material's yield stress for a particular slip system the dislocation will move along a path of least resistance occupying identical atomic sites until an obstacle, or slip inhibitor, stops its movement (or the shearing stress falls below that required for yielding). After the stress is removed the material will not regain its former shape; plastic deformation has occurred.

These dislocations tend to move most easily in certain planes and directions. And due to the random orientations of crystal nucleation and growth in metals, at any time many of these crystals will be oriented in pure shear relative to the applied stress. The shear stress required to move the dislocation is defined by the following Peierls- Nabarro equation;

$$\tau = ce^{-\frac{kd}{b}} \quad (1)$$

Where τ is the required stress to move the dislocation, d is the inter-planar spacing between adjacent slip planes, b is the magnitude of the Burgers vector and c and k are material constants.

Equation (1) shows that the stress required to cause deformation increases exponentially with the length of the Burgers vector. And the Burgers vector is least in directions which are closely packed. It is in these closely packed

directions on which slip is most likely to occur. The equation also shows that slip occurs most easily on planes that are far apart, that is where the inter-planar spacing is large, and the interatomic binding force is weakest.

Ageing aims to increase the energy required for slip systems to move through a material so that the only way plastic deformation can occur is by increasing the shear stress above the critical resolved shear stress (CRSS). Mechanisms used in the ageing process that increase the CRSS include introducing impurities within individual crystals, and increasing the total surface area of grain boundaries between crystals.

Of the three defects that occur in polycrystalline metals all are of importance in ageing; the line defects, or slip systems, are inhibited by introducing point defects through alloying (solute atoms within the host's atomic lattice). Surface defects are introduced by increasing the total area of grain boundaries by quenching, which produces smaller crystals. Moreover, on the subsequent ageing process hard non-equilibrium phase precipitates emerge from solid solution and add further strength and dramatically increase the energy required for slip systems to move around. Often aged alloys are further strengthened by work hardening before being placed into service.

Pre-ageing discussion

Dendrite development

Casting resulted in some solidification defects such as inter-dendritic shrinkage. Aluminium can shrink by as much as 7% on solidification (Askeland, 2011). All the alloys, from all stages of the experiment, displayed a dendritic structure and many displayed shrinkage defects.

Dendrites form on freezing as a result of heterogeneous nucleation, which is common in alloys lacking impurities; introducing impurities into a molten metal or alloy provides sites for nucleation (boron is often used for this purpose).

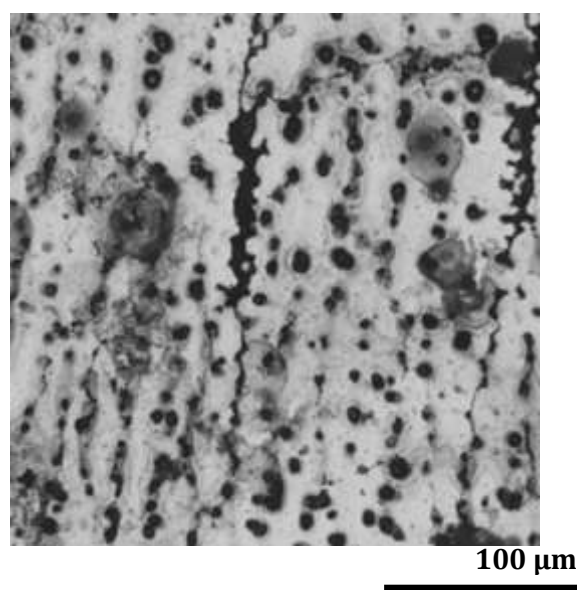


Figure 11; Sample showing inter-dendritic shrinkage defects.

The metals used were 99.99% pure and were thus poorly 'inoculated' meaning that there were insufficient impurities to allow homogenous nucleation which usually results in a planar type of grain structure. Instead, nucleation occurred heterogeneously on the mold walls, which provided a big enough temperature gradient for critically sized groups of atoms to develop into nuclei. After nucleation the grains grew inwards into the ingots as the liquid ahead of the dendrite tips froze. The dendritic structure of the cast ingots is in visible figure 9 above. Inter-dendritic shrinkage is noticeable as a vertical black continuous irregular line near the middle (another can be seen running into the top right hand corner of the image).

The desirable precipitates, by comparison, are discrete and rounded, although both features appear on grain boundaries (also vertical). Such shrinkage defects seriously limit the material's strength, especially should a shearing force be applied in the same plane as the defects that are all, more or less, parallel. The defects may have been caused by a low ratio of alloy volume to mold surface area giving a high rate of undercooling. Preheating the mold, and reducing the cooling rate, would have helped to avoid shrinkage defects. Also, alloys of this type are usually used in a wrought condition; a process such as rolling or forging, post-casting, would have helped to break up the parallel structure of the grains and defects, as well as giving further strength due to work hardening.

Solubility

From the phase diagrams appended, it can be seen silver has a relatively large solubility in aluminium at the eutectic temperature of the aluminium and copper binary system that was used for the solution treatment stage in this investigation. By weight, 47% (silver compared to copper's 5.65 %) can dissolve in aluminium at this temperature. The maximum solubility of silver in aluminium occurs at the eutectic temperature for that binary system (around 530°C) which is close to the maximum solubility of copper in aluminium at the eutectic for that system (just under 550°C).

This fact made silver and copper good candidates for a ternary aluminium alloy system as it allowed a super saturated solid solution (SSSS) to be created for both guests in their host using similar process parameters such as a suitable solutionising temperature, soak time, quench rate and ageing time and temperature. Silver atoms are around 40% bigger than aluminium, whereas copper atoms are around 23% bigger than aluminium (see A1), this causes strain in the atomic lattice improving strength even before the alloys were aged.

The solubility of silver and copper in aluminium drops dramatically with temperature under thermodynamic equilibrium conditions, as can be seen from the phase diagrams (see A4). The homogenisation was intended to create an equilibrium ternary system of regular grains, although the solubility of both guests had been well exceeded within the aluminium host. Hardness testing was conducted on the homogenised samples between 22 and 26°C. Under these conditions the solubility of both guest atoms was low compared to the quenched condition used for ageing which was intended to create a

solid solution with the maximum amount of guest atoms dissolved in the aluminium lattice structure.

Nevertheless, after homogenisation the alloys all displayed an increase in strength with silver content, despite the fact that the solubility limits were grossly exceeded. This was partly because of the strain induced in the crystalline FCC aluminium lattice as a result of the much larger silver and copper atoms taking up vacancies, thereby increasing the stress needed to move slip systems through the material.

It's possible that some of the strength increase observed after solution treatment is due to a phase of copper silver atoms, although no evidence was found for this. Such a phase is different to the α phase so far discussed as the guest copper atoms are now smaller than the host atoms; the result of these smaller substitutional atoms is still a strain within the atomic lattice but it is a contraction rather than an expansion.

Solid solution strengthening (SSS), and the formation of secondary intermetallic phases, are two mechanisms that have created an increase in strength in the alloys investigated here in the pre-ageing stages of the experiment. SSS occurs when the atoms of different alloyed constituents have different atomic radii. This creates a change of dimension, or strain, in the lattice. As a result more force is required to overcome the inter-atomic bonds and dislocation slip is inhibited. The degree of strengthening depends on two factors; the difference in atomic size and the amount of the guest atoms dispersed in the host.

Optical microscopy revealed Ag rich precipitates on grain boundaries after homogenisation. In the image below on the right, the silver rich precipitates have nucleated at the grain boundaries on Guinier Preston sites and grown following the lines of the grain boundaries. No such linear structures are visible in the left hand image which contains no silver.

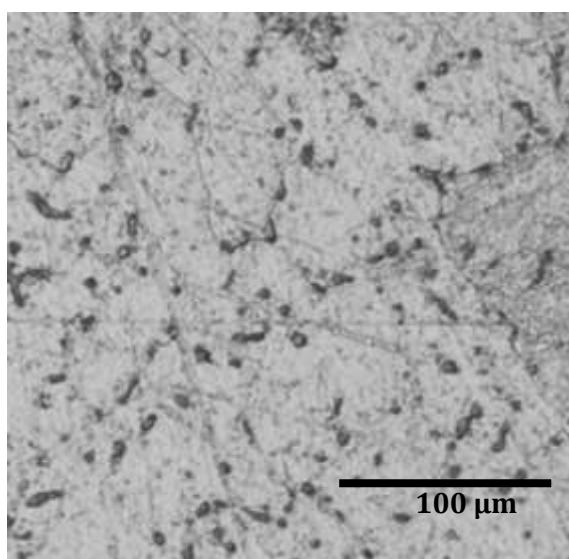


Figure 12; homogenised 0% Ag.

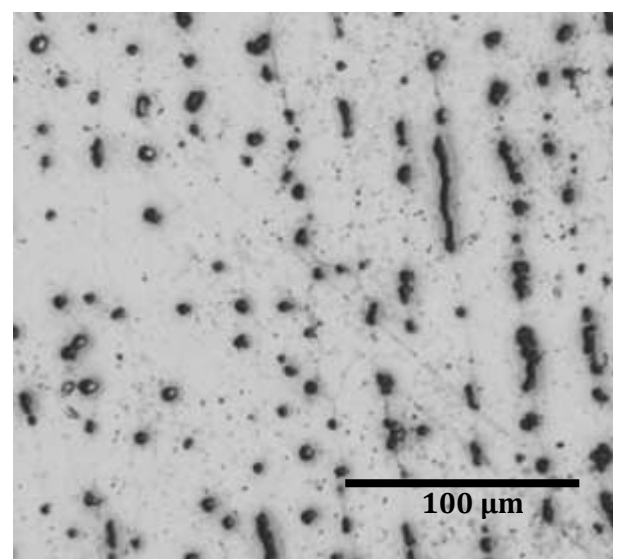


Figure 13; homogenised, 7% Ag

For the sake of consistency, all the microscopy images presented in the paper have been taken from close to the middle of the sample and orientated on the same axis (with the top being towards the surface of the ingot). Ag rich precipitates have nucleated on the grain boundaries as these sites give the highest energy for diffusion to occur most easily. It can be seen that precipitates have grown until forming long chains of linked precipitates.

Research on other aluminium alloys has shown that that the precipitates in aluminium alloys often nucleate on {111} planes. This research also concluded that if too much alloying element is used the precipitates can develop with extreme shape anisotropy (Martin, Doherty & Cantor, 1997).

Many of the homogenised samples with silver display a similar micro-structure to that in figure 10 in which the precipitates (which appear black as they have been attacked by the nitric acid during etching) have formed linear features running from top to bottom; that is across the thinnest part of the cast sample following grain boundaries. These precipitate rows become more pronounced as the content of silver increases as can be seen by comparing figure 13 with figure 14, which contains only 3% Ag.

Such long chains of precipitates are not desirable! One of the strengthening mechanisms of precipitates is their ability to 'pin' the grain structure together; should these Ag rich alloys be employed in such a manner that a shearing force acted parallel to them it is possible they could provide a hard inter-granular surface over which the grain structure could move.

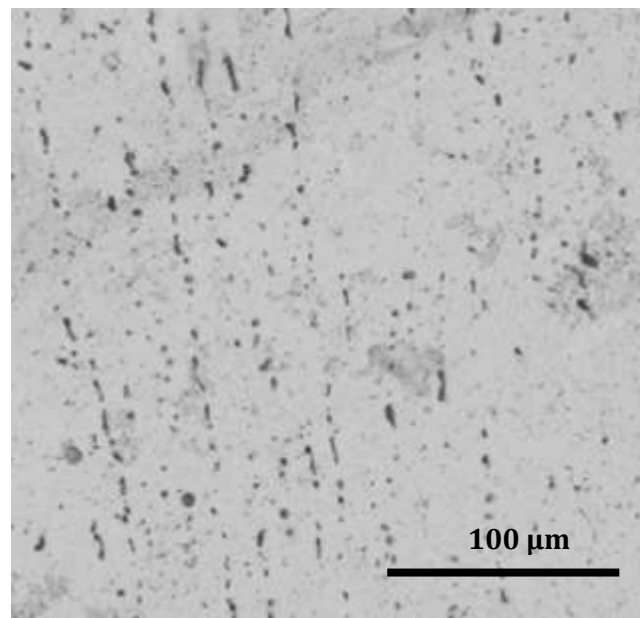


Figure 14; Homogenised 3% Ag

It should be noted that it is usual to employ alloys such as this in the wrought state, and such processing would certainly help to disrupt the parallel alignment of the precipitate rows (Martin, Doherty & Cantor, 1997).

It is possible that some 'coring' has also occurred during homogenisation; on cooling sub-phases with the highest melting point appear to have frozen first (following the lever rule) and subsequently there has been insufficient energy/time for diffusion of these non-equilibrium sub-phases into the equilibrium phases desired for homogenisation to be completed. This suggests that further work is needed to optimise process parameters.

Post-ageing strength increase

The ageing process depends on diffusion. The non-equilibrium super saturated solid solution decomposes to form hard precipitates by diffusion. The formation of these precipitates is both time and temperature dependent where D , the diffusion coefficient is related to temperature by an Arrhenius type relationship.

$$D = D_o \exp\left(-\frac{Q}{RT}\right) \quad (2)$$

Where Q is the activation energy in calories/ mole, R is the gas constant (1.987 calories/mole.Kelvin) and T is the absolute temperature (Askeland, 2011).

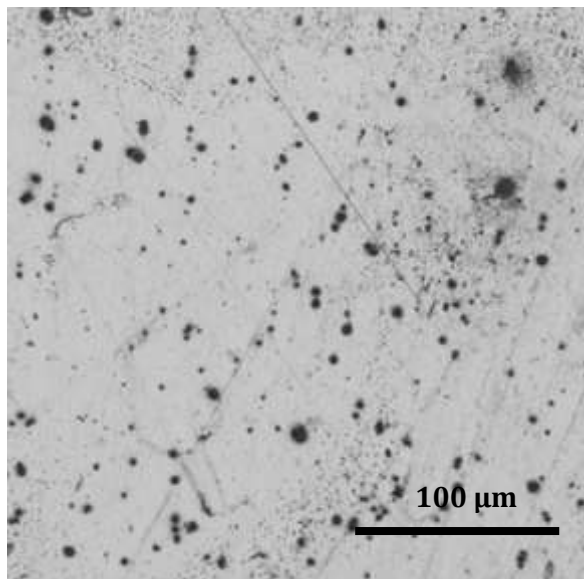


Figure 15; solution treated Ag 8%

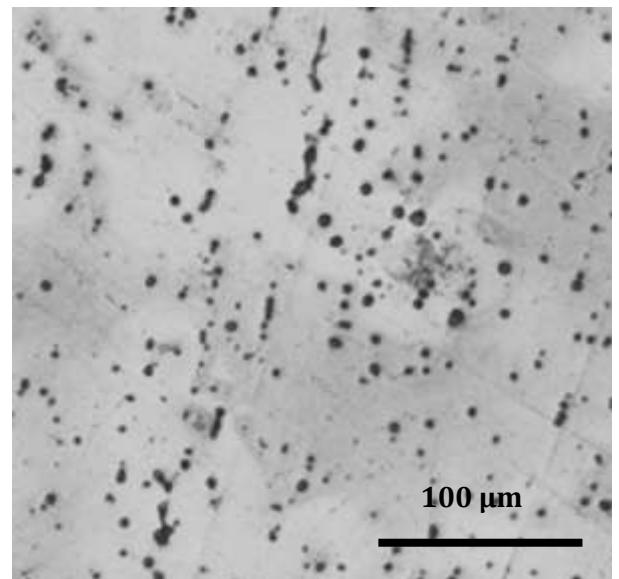


Figure 16; aged 4 hours, Ag 8%.

The figures above shows the 8% Ag alloy after solution treatment (left) and after ageing for four hours. The increase in precipitates after ageing is clearly visible.

The image on the left shows that precipitates were already present in the solution treated samples (when the picture was taken). Reasons for this may include; the rate of cooling was not fast enough to keep all the constituents in solution; or the percentage of silver (8%) was too high and the aluminium matrix was saturated (although this does not appear to be the case; Ag has more than 40% solubility in aluminium at the solution temperature used).

A more likely reason for the unexpected presence of precipitates in the solution treated samples was that the ageing process was already well under way when microscopy was carried out, more than a week after solution treatment. The investigation also confirmed that the decomposition of precipitates is a function of time, as implied by equation (2).

Figures 17 and 18 show how time has effected the decomposition of the super saturated solution; the precipitates in the right hand image (aged 4 hours) are more pronounced as they have had longer to grow.

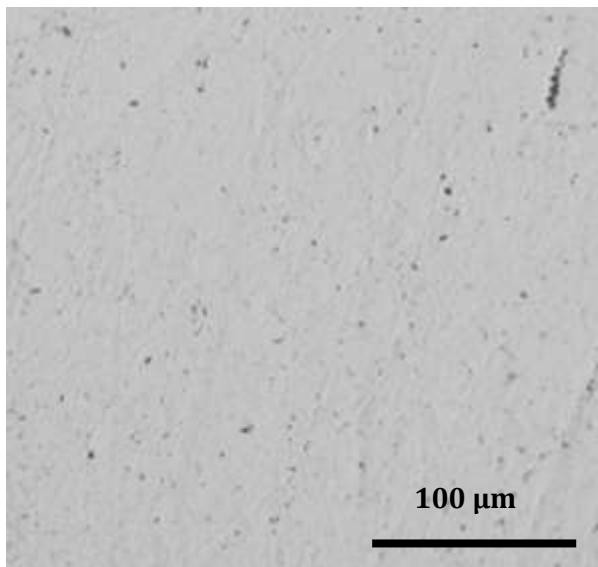


Figure17; 3% Ag aged 2 hours.

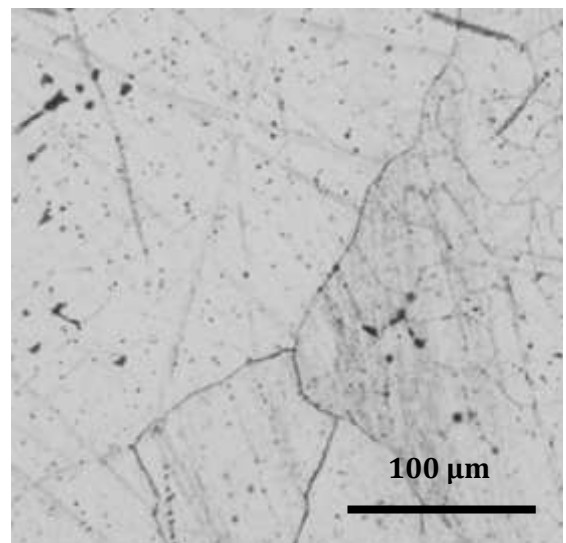


Figure18; 3 % Ag aged 4 hours.

Energy for Diffusion

Quenching used during the solution treatment gives little time for grain growth to occur resulting a small grains and a relatively large surface area of grain boundary (in fact if the quench rate is high enough a metallic glass like structure can result). This results in a much higher concentration of possible nucleation sites for precipitation growth. (Askeland, 2011). The mechanism by which atoms move to form such precipitates is diffusion. A saturated solution suitable for ageing can only be created by cooling the alloy at a rate which is faster than the critical cooling rate for diffusion into a state of thermodynamic equilibrium to occur.

Further, the value of Q is a function of melting point; the higher the melting point the more energy is required to overcome the atomic bonds. It can be seen from the equation above that as Q increases D decreases exponentially. Thus, because Q increases with the melting point of the alloying guest element, in the ternary system under consideration we can say that for copper/ aluminium diffusion the value of Q is higher than that for silver /aluminium. The corollary seems to be that ageing in the system under consideration will produce precipitates that contain aluminium and silver more

readily than precipitates that contain combinations of aluminium and copper atoms just because the value of Q is lower for that binary system.

This idea was investigated by spot analysis using a scanning electron microscope using back-scatter X-ray. Figure 15 shows the sample aged for 2 hours with 8% Ag. The data collected from spots 22 and 23 on the sample surface is presented below.

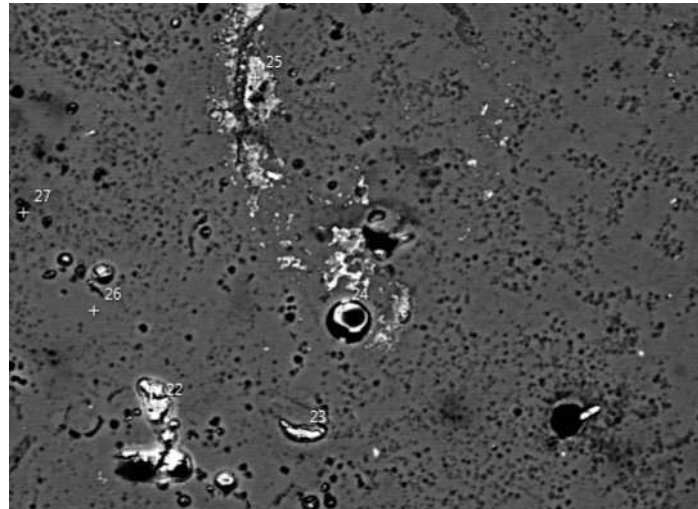


Figure 19; SEM image of the sample aged 2 hours with 8% Ag

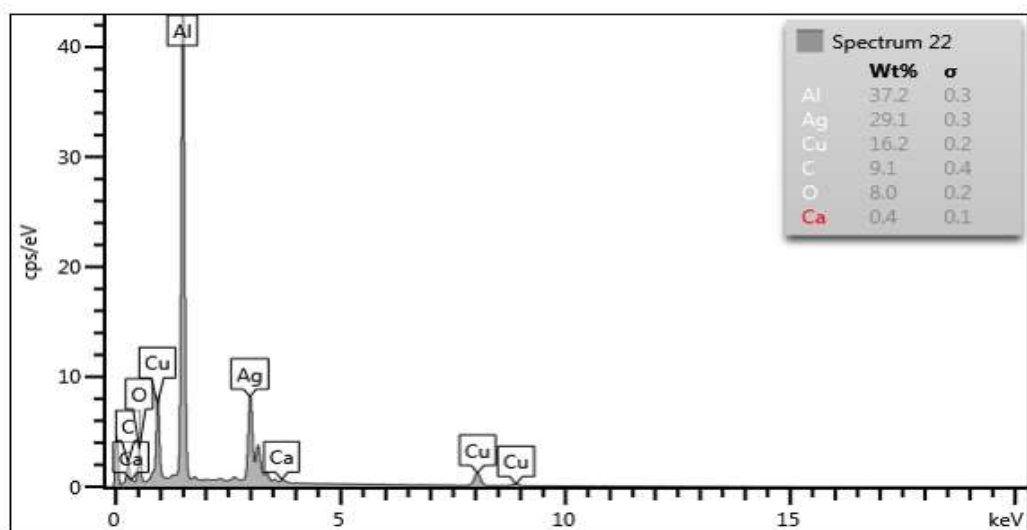


Figure 20: spot analysis of a precipitate in the sample aged for 2 hours, with 8 % Ag.

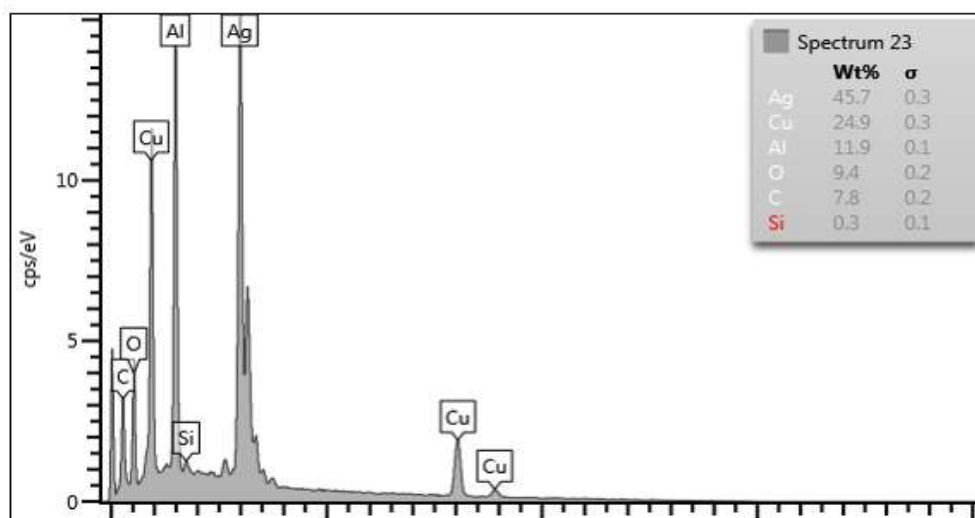


Figure 21; spot analysis of a precipitate in the sample aged 2 hours with 8% Ag

When the percentage weight of silver reaches around 7-8% the number of silver atoms present is about the same as those of copper (this is discussed in more detail later). For this reason the 8% silver alloy was investigated to determine which guest element more readily diffuses to form precipitates. In both figures above, it can be seen that the SEM has identified far higher concentrations (by weight %) of silver than copper at the site of precipitates, which appear lighter in colour when the microscope is in X-ray backscatter mode. However, when considered in terms of atomic % the spots analysed at sites 22 and 23 are surprisingly balanced in terms of silver and copper content.

Analysis on the darker matrix shows this to be rich in aluminium with silver around 4-9% and copper in similar proportions. Analysis on all spots revealed the unexpected presence of carbon, possibly coming from the Bakelite sample mount, or contamination in the SEM column. It is, however, over simplistic to conclude that any ternary alloy will decompose into precipitates with lower Q values more readily than those with higher values. This is because other factors affect diffusion, such as the concentration gradient (according to Fick's first law) and the lattice structure of the alloy; diffusion occurs more easily on closely packed planes in face centred cubic (fcc) crystal structures than in body centred cubic (bcc). Also, of the mechanisms by which diffusion occurs (vacancy, substitutional and interstitial diffusion) interstitial diffusion requires the least energy to achieve.

Research has shown that lattice structures other than fcc can occur in aluminium alloys. Even small amounts of Ag and Mg (< 1% weight) added to an aluminium alloy containing 4% Cu by weight promoted the development of a precipitate with an hexagonal close packed (hcp) structure (denoted as Ω phase) at the expense of the θ' phase usually associated with Al/Cu alloy systems (Scott, Kerry & Trumper, 1987).

Other research has found that all phases in the A1 regions of the ternary system in question have fcc lattice structures meaning that diffusion occurs more readily than in bcc lattice structures (Witusiewicz *et al.*, 2004).

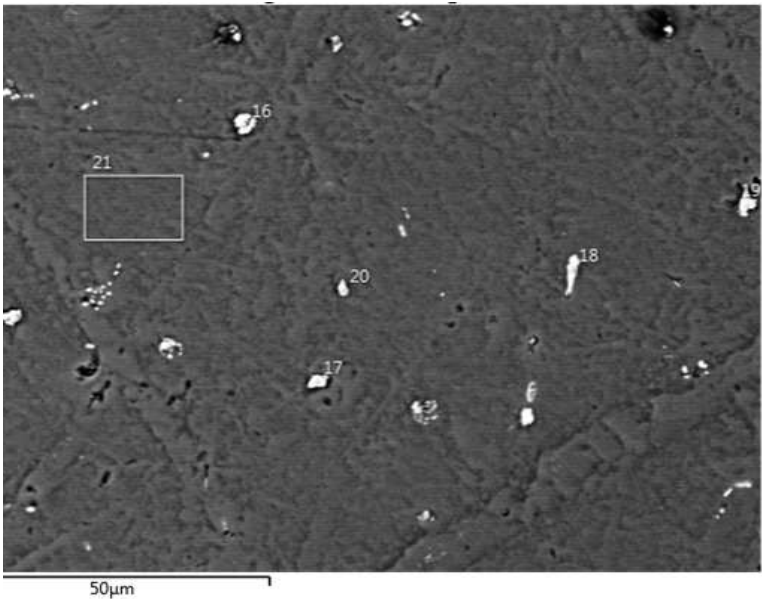


Figure 22; SEM image of sample aged 2 hours, Ag content 2%

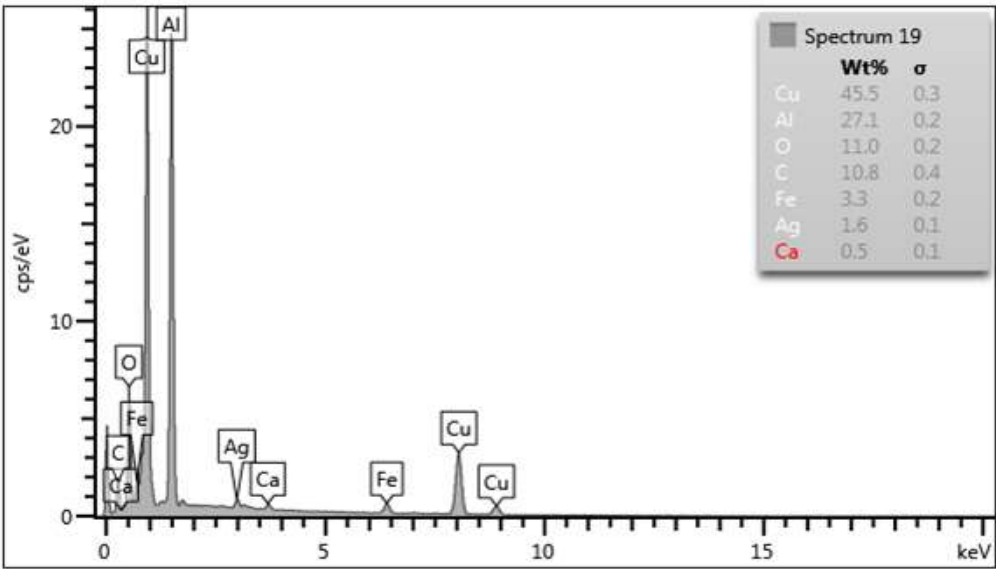


Figure23; SEM spot analysis of a precipitate in a sample aged 2 hours with 2% Ag

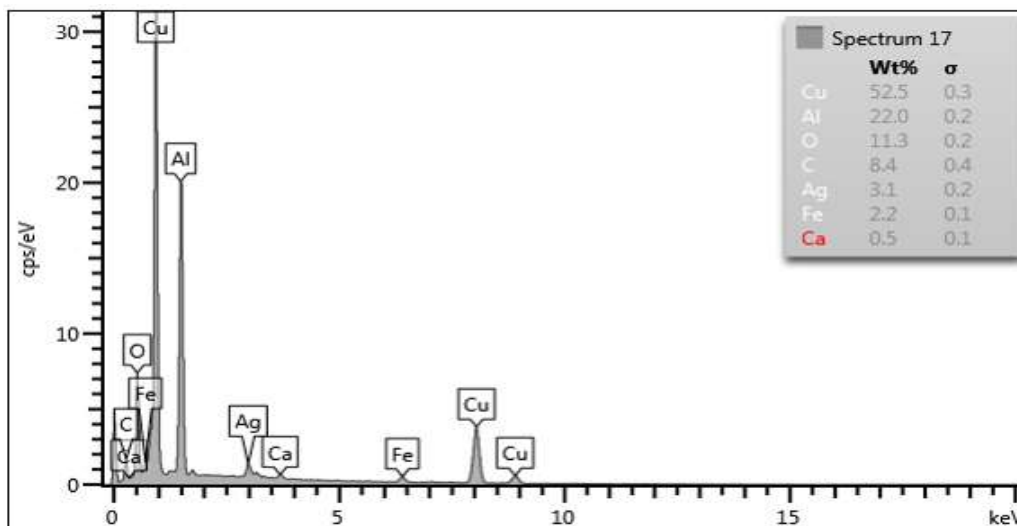


Figure 24; SEM spot analysis of a precipitate in a sample aged 2 hours with 2% Ag

X-ray spot analysis on the alloy sample containing 2% Ag and aged for 2 hours (figures 22, 23, 24) reveals that most of the precipitates that formed are rich in copper. Due to the difference in atomic mass and density of copper and silver it is only when the silver content (by weight) exceeds approximately 1.6 that of the copper that the number of atoms present for each is more or less equal (see appendix A5). Placing that into context for this investigation; of all the alloys manufactured only those with more than 7-8 % silver contain more silver atoms than copper

Thus, for the reasons just discussed it is not surprising to find the precipitates are rich in copper and little silver has been detected on by the electron microscope in the image above showing the sample with 2% Ag, aged for 2 hours (figure 22). The precipitates form as guest atoms diffuse from lattice sites in the host matrix to nucleation sites. In doing so they must overcome the strain energy present due to the difference of atomic size between guest and host; the strain energy holding silver atoms in place within the aluminium host is bigger due to there being a larger difference in size between silver and aluminium and copper and aluminium (see Appendix 1 for atomic data).

Diffusion rates also depend on the concentration gradient of atoms; for this reason it is worth considering the atomic proportions of the alloys rather than the weight percent.

Phases Present

Given that the material under investigation is a ternary system the possible combinations of elements that could decompose into precipitates is three, two of which AlAg_2 (γ') and Al_2Cu (θ') have been identified and researched in some detail (Rosalie, *et al*, 2011). That research has shown that during aging a continuous series of precursor precipitates form before the final phase has developed on Guinier-Preston (GP) sites.

This investigation has not found any precipitates consisting of silver and copper only, and a literature review found no evidence that other research has found such a phase in the ternary system investigated here. During ageing precipitates emerge from the solid solution α phase by nucleating on grain boundaries at GP sites. The appearance of discrete non-coherent θ' precipitates is both time and temperature dependent. Their non-coherence is desirable as this makes them more efficient at preventing slip.

The process by which the precipitates develop has been researched in depth and has been shown to be quite complex even in relatively simple binary systems such as aluminium and copper (Ringer & Hono, 2000). In ternary systems the same research has shown that if the conditions permit the ageing process will continue until a coherent θ phase develops; this happens because this is the phase with the lowest energy. Once the equilibrium phase has established the alloy is said to be over-aged. In the over aged state the coherent θ phase is less effective at preventing slip and the material's strength begins to drop (Askeland, 2011).

Conclusions

- 1) The alloys continue to increase in strength across all stages; this implies that the alloys were not over aged by the parameters used.
- 2) Small increases in strength with content Ag may be deemed to be not viable commercially due to the high cost of silver.
- 3) Similar strength properties are attainable with alloys of this ternary system than other aluminium alloys currently available, but only in a wrought condition. It is also apparent that the material, all other things being equal, would be disadvantaged by its specific strength, due to silver's high density.
- 4) Alloys of this kind are not suitable for high temperature applications because the ageing process depends on diffusion, which in turn depends on temperature; at elevated temperatures the alloys will quickly over age and their material properties are adversely affected as the desirable non-equilibrium precipitates reach their equilibrium.
- 5) Keller's Etchant is unsuitable for alloys with silver in them; the nitric acid appears to attack the silver aggressively.

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